Processing Improvements for Roll-to-Roll Deposition of Cu(InGa)Se2

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ABSTRACT

In this paper work on in-line processing of $Cu(InGa)Se_2$ performed under Task 2: CIS-based Solar Cells of our Thin Film Partnership program, "Processing, Materials, Devices and Diagnostics for Thin Film Photovoltaics: Fundamental and Manufacturability Issues" is presented. Cracking of Mo and adhesion of the $Cu(InGa)Se_2$ film to the polyimide web have been a critical issues in making flexible modules. By incorporating O_2 into the Mo back contact layer and by controlling the Se delivery rate during $Cu(InGa)Se_2$ deposition, crack free and good adhesion are demonstrated. Another critical problem has been the design of the metal evaporation sources for high delivery rates needed for manufacturing. Using a modified source design rates 5 times higher than required for manufacturing are presented.

1. Objectives

The objectives of this research program are to develop the in-line deposition of $Cu(InGa)Se_2$ films from elemental evaporation sources onto moving Mo-coated polyimide substrates at rates commensurate with commercial manufacturing. Additional goals are to determine the effects of Ga and In distributions, Na incorporation, and improved substrate temperature control. Critical problems with Mo cracking, poor adhesion, and source design were identified and have been the primary focus so that these objectives can now be addressed.

2. Technical Approach

The scale-up of multi-source $Cu(InGa)Se_2$ (CIGS) vapor deposition on polymer substrates at commercial throughputs introduces a number of issues not encountered in lab-scale stationary systems. Two of these are the design of high-rate evaporation sources (> 10 g/hr) and the development of a Mo back contact deposition process that would eliminate film cracking during CIGS deposition [1-4]. Resolution of these issues is the first step towards the commercialization of flexible CIGS photovoltaics.

The present investigation was performed in an inline CIGS deposition system having a roll-to-roll web transport mechanism where both tension and speed are adjustable. Metal sources were linear crucibles having two evaporation nozzles. They were positioned perpendicular to the machine direction and centered around the deposition zone in Cu-Ga-In order. Se was evaporated through a manifold with holes evenly distributed among the metal sources. A 50 micron thick Upilex S web coated with ~0.2µm Mo was maintained at 425°C. A more detailed description of the system was given previously [5].

3. Results and Accomplishments

Source Spitting

Original sources designed with cylindrical nozzles sticking up from the BN boats worked well for Ga and In but in the case of Cu caused spitting. This spitting action, which was observable by the naked eye resulted in Cu inclusions in the CIGS film ultimately causing shorting of the devices. It was observed that the spitting increased with the effusion rate and was totally suppressed when the effusion nozzle was reduced to a hole on the lid of the source boat. These observations seemed to indicate that, phenomenologically, the temperature drop along the effusion nozzle is responsible for the spitting. Thermal modeling of the nozzles of various shape indicated that an externally tapered nozzle would result in the lowest temperature drop by increasing heat flow to the nozzle tip. When such a nozzle geometry was incorporated into the Cu evaporation boat no spitting or inclusions were observed. Figure 1 gives the schematic nozzle geometries and the corresponding photographs of Cu effusion from the nozzles. The 45° tapered nozzle, shown at the bottom, was operated

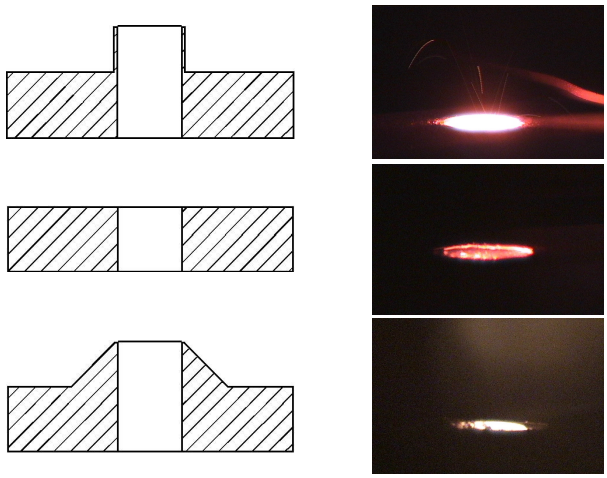

Fig. 1. Nozzle geometries and the corresponding view of the effusion of Cu.

at 15g/hr effusion rate while in the other two cases the effusion rate was 2.8g/hr. A thermal model gives a temperature drop of 14°C along the tapered nozzle, and a drop of 33°C along the inside wall of straight nozzle shown at the top of Figure 1. It should be pointed out that though the tapered nozzle geometry solved the spitting problem the actual mechanism of spitting is still not well understood.

Film Cracking

During the course of investigating Mo films, deposited on Upilex S under various conditions, for their propensity to cracking during CIGS deposition it was observed that crack density decreased dramatically when Se usage per run was reduced. At the same time, CIGS films deposited under reduced Se condition showed better adhesion to the Mo layer as evaluated by a pull test using 40oz/in tape. As a result it was postulated that chemical reaction between Mo and Se is responsible for the mechanical weakening of the Mo layer causing it to crack. No evidence of such a reaction was found when the Mo layer, after the removal of the CIGS layer, was analyzed by glancing incidence XRD. This however, may not be a sufficiently sensitive technique to very thin layers or to reaction byproducts residing predominantly in the grain boundaries. To reduce chemical reactivity of the Mo to Se, O_2 was added into the Mo layer. The Gibbs free energy of formation of the most stable molybdenum selenide, Mo_3Se_4, is –363kJ/mole while that of the least stable molybdenum oxide, MoO_2, is –467kJ/mole.

Three different Mo deposition conditions were evaluated. In the first case, standard Mo was deposited on Upilex S while the heat load on the web was conductively removed by a backing drum. In the second case, oxygen was added to the Ar sputtering gas. The third condition was the same as the first one except that the web temperature was allowed to increase by not actively removing heat load from the sputtering plasma. Preliminary Auger analysis showed that in the first case the oxygen concentration in the Mo film was around 3at%. On the other hand oxygen levels of around 8at% were found in the Mo deposited under the other two conditions.

The inspection of CIGS films showed heavy cracking on the standard Mo substrate while no cracking could be found on the other substrates. Devices were fabricated on these CIGS films in order to evaluate the CIGS more quantitatively. Devices on the standard Mo substrate had efficiencies less than 3% due to the cracked Mo while devices on the substrates where Mo was deposited at high temperature or with O_2 had efficiencies between 9 and 10%. Auger analysis of the Mo films indicated that the substrates with Mo deposited without tension or with O_2 contained about 8% O_2 while the standard Mo deposition had less than 3% O_2.

In addition, spatial uniformity of the devices was evaluated on one of the runs made on Mo deposited at high web temperature. Four devices were fabricated on each sample taken approximately every 10" in the machine direction. Table I gives the average device parameters for each sample along with the grand average of all the devices. The uniformity of the performance is remarkable until 50" from the leading edge. Pass that point there is a small but measurable drop in performance. It is believed that this drop is probably due to depletion of the Se source.

Table I. Average solar cell device parameters from samples taken along the web.

Position from leading edge (in)	Eff. (%)	V_{OC} (V)	J_{SC} (mA/cm^2)	Ff (%)
10	10.6	0.501	64.8	32.7
20	10.2	0.505	62.4	32.5
30	10.2	0.504	62.4	32.4
40	10.0	0.501	61.7	32.4
50	9.6	0.501	58.3	32.9
60	8.1	0.517	49.8	31.5
Average	9.8	0.505	59.9	32.4
Standard Dev.	0.9	0.006	5.3	0.5

4. Conclusions

Solutions have been presented to two major problems that have hampered the development of large scale deposition of CIGS films on flexible substrates. Eliminating spitting from the Cu source enables the use of high effusion rates necessary for increased throughput. Incorporating oxygen into the Mo back contact, solves the problem of film cracking which was, until now, a show-stopper in the development of flexible CIGS photovoltaics.

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